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CONTINUOUS PROCESS FOR PRODUCING PELLETIZED
NITROCELLULOSE

NAVAL ORDNANCE STATION

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by

R. C. Wilson

T. Liggett

G. C. Cox

J. E. Geist

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NAVAL ORDNANCE STATION

Indian Head, Maryland

S. P. GARY
Captain, USNavy
Commanding Officer

JOE L. BROWNING
Technical Director

FOREWORD

This report covers two manufacturing technology projects which were performed at the Naval Ordnance Station, Indian Head, Md., for the Naval Ordnance Systems Command, Industrial Resources and Equipment Office (ORD-047). P. O. 8-0199 of 23 October 1967 and P. O. 9-0295 of 9 December 1968 funded the development and verification of a process for continuous production of pelletized nitrocellulose; WR 2-6103 of 19 June 1972 funded process optimization techniques. The objective was to develop and install a system that would provide a source of pelletized nitrocellulose for automated processing of propellants and explosives in anticipated quantities and at a reasonable cost.



D. H. Carstater

Manager, Advanced Products and
Processes Branch

Approved by:

J. L. Tomlinack
Director, Pilot Plant Division

Released by:

J. E. Henderson
Head, Ordnance Department

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ABSTRACT

Pelletized nitrocellulose is a special form of nitrocellulose having a uniformity of size and shape that provides excellent formulation and processing characteristics. It has been prohibitively expensive for many applications in the past, but new manufacturing technology has reduced the cost drastically.

The technology developed for continuously manufacturing pelletized nitrocellulose from a nitromethane-nitrocellulose lacquer, and the operation of the resulting pilot production system which has been installed and is operating at the Naval Ordnance Station, Indian Head, Md., are described in this report. Environmental pollution has been virtually eliminated and improved product quality has been obtained. The cost of manufacturing pelletized nitrocellulose in quantity has been reduced to less than 25% of the conventional batch process costs.

INTRODUCTION

Pelletized nitrocellulose (PNC) is a special form of nitrocellulose in which the fibrous material has been physically altered to form spheres having an average particle size of 5 to 50 microns. The spherical material having free flowing characteristics greatly improves both the mechanical handling of the nitrocellulose and the mixing of a propellant or explosive containing this ingredient. As a result, it imparts a higher bulk density to the mixture and provides a better cohesive bonding characteristic upon cure than the normal fibrous material.

PNC is manufactured to meet the specifications of WS 12799. It can be produced from nitrocellulose of five different grades having a nitrogen content ranging from 12.00% to 13.25%. The starting nitrocellulose is required to have been produced from cotton linters cellulose. However, PNC has been successfully manufactured from nitrocellulose of wood pulp origin. There are five classes of PNC with particle sizes ranging from 8 to 40 microns. (Particle size is determined by a Sharples Micromerograph.)

PNC is a key ingredient in advanced, slurry cast, modified double-base explosives and propellants, or other propellants employing a nitrocellulose matrix binder where the PNC is either crosslinked or combined with an advanced plasticizer. PNC is a required ingredient in PBXN-103 explosive used in the Torpedo Warheads MK 103 and Mk 107 and has forecast needs in candidate Quick Strike Mine and SGP-type double-base gun propellant. Although other forms of nitrocellulose can be used in some of these formulations, larger amounts of the particulate nitrocellulose are required to obtain similar bonding properties. This results in a decrease in the available energy in the composition, other ingredients being the same.

Slurry cast, composite-modified, double-base compositions have widespread interest in the United States because of their simplicity of manufacture and high potential performance in both propellants and explosives. Their continued growth of application depends on moderately priced sources of high quality, spherical (5 to 50 micron) nitrocellulose. Castability, adequate pot life, and good mechanical properties of the finished compositions are important criteria of merit for slurry cast systems. All of these criteria are highly dependent on the nature of the nitrocellulose, plasticizers, and solids loading.

The Naval Ordnance Station, Indian Head, Md., has produced PNC by a batch process for more than a decade, and this material has been shown to impart physical properties superior to those produced in compositions incorporating other specialized nitrocellulose forms. Current prices for industrially supplied materials range from \$3.50 to \$20.00 per pound depending, to a degree, on the quantity requirements. PNC produced at Indian Head by the conventional batch process has ranged between \$15.00 and \$22.00 per pound in costs.

High PNC costs are attributed to the loss of solvent used in processing, 20% to 25% product loss in filtrate during product recovery, and the labor inefficiencies generally associated with batch-type processes. To substantially reduce the manufacturing costs and to improve product quality, Indian Head undertook a program to establish a continuous automated PNC pilot process with solvent recovery capability. Also by establishing the new processing facility, the industrial readiness to supply PNC could be increased.

The objective was achieved through laboratory and small-scale processing studies of operating variables, techniques, equipment, and intermediate materials to obtain essential industrial-scale process design data. The processing facility was successfully started up in September 1972. Evaluation of the new process shows that PNC can be manufactured in quantity from \$1.50 to \$3.00 per pound.

PROCESS DESCRIPTION

Continuous Processing

The newly installed, continuous PNC process (Figure 1) involves, first, making a lacquer by dissolving water-wet (20% minimum) virgin nitrocellulose in nitromethane. This is done in hot-water jacketed vessels equipped with agitators and baffles. The contents are heated to 140° F and complete dissolution takes place in about 3 hours. The lacquer is pumped at a measured rate into the system. The nitrocellulose lacquer feed is continuously and vigorously mixed with a small quantity of water at 120° F containing 4% to 8% nitromethane at the inlet of an emulsifier. Emulsification is completed in a single pass through the mill. Immediately following emulsification, the stream is drowned or quenched in a continuous manner using a pipe "tee" with a relatively large volume of water controlled at about 120° F. This extracts most of the nitromethane from the lacquer which was formed into small spherical droplets as the dispersed phase during emulsification. The drown solution used in this process is actually filtrate recycled from the product recovery system. As this filtrate contains some fines, product losses are minimized. The drowning is accomplished continuously with

vigorous mixing occurring through stream turbulence where the streams meet at high flow velocities. After entering a surge tank and allowing sufficient residence time for the drowning extraction to reach equilibrium, the mixture is pumped to the drown column.

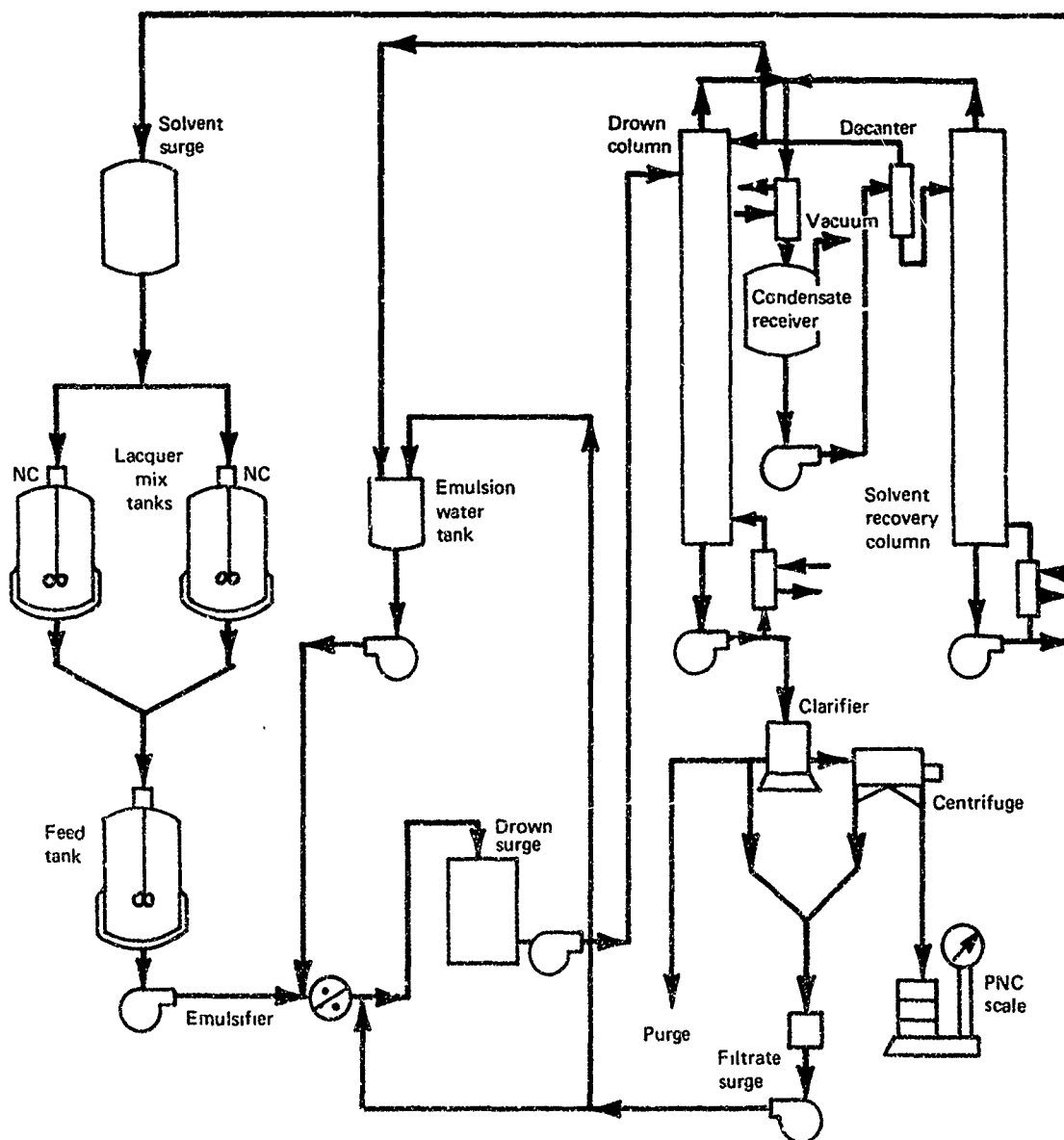


FIGURE 1. CONTINUOUS PELLETIZED NITROCELLULOSE PROCESS

First Distillation:

The process stream enters the down column in a water-rich zone where precautions are taken through careful temperature control to ensure the absence of free nitromethane. The PNC-water slurry flows to the bottom of the column where it is circulated through a reboiler. A portion of the water is evaporated, becoming the driving force, and is carried up and refluxed within the column to strip the nitromethane (as an azeotrope with water) from the bulk of the down stream. The down column also is the first distillation column in the two-step distillation required to recover nitromethane. The column is operated at 230 torr.

Product Separation:

A side stream of the PNC-water slurry is taken off the down column bottoms circulating pump to maintain the desired operating level in the column. This side stream is fed to a disc, bowl-type, centrifugal clarifier where the slurry is concentrated from about 0.4% solids to about 2.3% solids. The clarifier effluent, containing less than 50 ppm solids, flows by gravity to the filtrate surge tank. The concentrated slurry flows by gravity to a solid bowl continuous centrifuge. The PNC product, wet with 35% to 40% water, is discharged into drums, weighed, and removed from the area. The centrifuge filtrate, containing less than 0.4% product fines, also flows to the filtrate surge tank. The bulk of the hot water filtrate is cooled and reused in the process as down water. A considerably smaller portion is pumped to the emulsion water tank for emulsion water makeup. Any excess filtrate overflows to a catch tank and is purged from the system, thus minimizing accumulation of soluble impurities in the process. The overall water balance is maintained through periodic water washdowns of the separation system.

Second Distillation:

The azeotrope (containing 21.3% water at 200 torr) from the down column is condensed and pumped to a decanter where it separates into two layers. The top (water-rich) layer containing about 9.5% nitromethane at ambient temperature is returned as a reflux to the down column. The bottom (nitromethane-rich) layer containing approximately 2.3% water is drawn by vacuum into the nitromethane recovery column. The recovery column is operated at 315 torr. The water-nitromethane azeotrope removed overhead is condensed with the azeotrope from the down column. Dry nitromethane is removed from the column bottom and pumped to a storage tank for reuse in lacquer makeup.

U. S. Patents 3,671,515 and 3,702,353 of 20 June 1972 and 7 November 1972 were awarded for the unique concepts of this continuous PNC process and the basic changes in processing techniques.

Batch Processing (Comparison)

The first step of the conventional batch process (Figure 2) is similar to the continuous system where a nitromethane-nitrocellulose lacquer is prepared in a solvation tank. At the second step of the batch operation, a pre-emulsion containing specific quantities of lacquer, water, and a surfactant is batch-prepared in a second tank. The water and surfactant are mechanically agitated throughout the period of lacquer addition and until the entire mixture has been pumped through a colloid mill. From the colloid mill, the emulsified stream flows into a large tank nearly full of water under agitation. Here drowning is accomplished. The temperature is maintained at 110° F in each vessel by hot water jackets or coils.

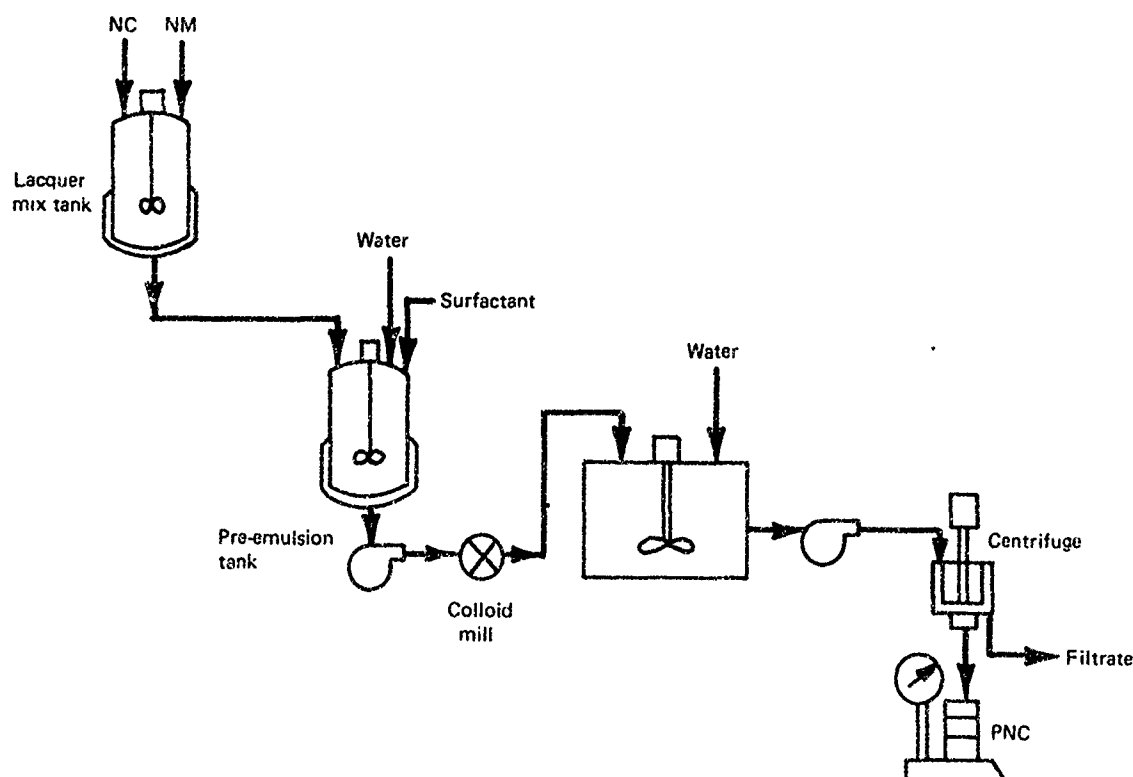


FIGURE 2. BATCH PELLETIZED NITROCELLULOSE PROCESS

After dewatering has been completed, the contents are pumped to a vertical, solid bowl, batch centrifuge. The filtrate, containing the bulk of dissolved solvent and a substantial amount of product fines, is discarded. Processing of a single 100-pound batch requires about 8 hours. The product contains a small quantity of residual solvent and tends to form agglomerates during drying. For specific uses, this plastisol grade nitrocellulose requires micropulverization prior to further processing, whereas the new (continuously processed) product, being free of nitromethane, does not.

Continuous Processing Advantages

The following are the salient advantages of the new process:

- (1) High material recovery and essentially no discharge of waste products or environmental pollutants as the result of a nearly closed system
- (2) Safer operating conditions through a reduction in material handling requirements and exposure of personnel to solvent fumes
- (3) Improved product quality control through the inherent internal blending characteristics of the process
- (4) Lower product costs owing to substantial reduction in material and labor requirements.

In general, the new material has shown decided improvement over batch-produced PNC in propellants. These improvements included higher tensile strength and better cure, elongation, and stability, while eliminating high cost, material particle adhesion, and significant quantities of contaminants (surfactant and solvent).

PROCESS DEVELOPMENT

The first phase of the program involved performing laboratory tests and small-scale batch studies to obtain data essential for the basic process design.

Hydrocarbon Media Studies

Basic distillation and solubility information concerning binary nitromethane-water and ternary nitromethane-water-hydrocarbon (hexane and heptane) systems was obtained from literature and laboratory experimentation. Work being done at

the time, with the inert-diluent process on the development of a wet solids feeder, indicated a future potential for hexane-wet and heptane-wet PNC. Tests showed that the regular nitrocellulose lacquer-water emulsion could be drowned in hexane or heptane to produce PNC of comparable quality to that resulting from water drowning. Employment of this system would yield PNC wet with the hydrocarbon that could be fed directly into the inert-diluent process, thus eliminating the regular and costly intermediate step of tray drying.

Operation of this system would require the recovery and reuse of the hydrocarbon in addition to the nitromethane. In the drowning distillation step, the PNC would migrate to the still bottom with the hydrocarbon while the distillate would form a ternary azeotrope (Table I) which separates into three layers (Table II). As in the water drowning system, nitromethane would be recovered from the bottom of the second distillation system. The hydrocarbon layer would be re-fluxed preventing buildup. The water layer, being acceptably low in nitromethane, is recycled to emulsification. The process design included basic details for adapting the ternary system.

The binary azeotrope from the nitromethane-water system boils at 83.6° C at atmospheric pressure and contains 77.1% nitromethane by weight. As previously noted, the condensed azeotrope separates into two layers. There is a small change in these compositions when the ingredients are distilled at 200 torr pressure as the azeotrope then contains 78.7% nitromethane.

Table I

TERNARY AZEOTROPIC DISTILLATION DATA

Drowning system	Conditions		Azeotropic composition (wt. %)			
	Temperature (°C)	Pressure (mm Hg)	Heptane	Hexane	Nitromethane	Water
Hexane	49-50	758	-	81.9	14.4	3.7
	24-25	200	-	85.2	12.3	2.5
Heptane	61-62	759.2	64.7	-	27.3	8.0
	37-38	200	65.6	-	27.7	6.7

Table II
TERNARY AZEOTROPIC CONDENSATE DATA (At 20°C)

System	Rich layer	Layer composition (wt. %)				
		Hexane	Heptane	Nitromethane	Water	Impurities ¹
Hexane	Hexane	97.08	-	2.57	-	0.35
	Nitromethane	1.48	-	85.35	2.71	10.32
	Water	-	-	9.43	89.70	0.86
Heptane	Heptane	-	97.70	2.30	-	-
	Nitromethane	-	0.29	91.08	2.52	6.11
	Water	-	-	9.48	90.52	-

¹ Impurities are essentially other nitroparaffins which are present in the starting nitromethane.

Effect of Vacuum on PNC Formation

A laboratory test was performed to determine if vacuum stripping of nitromethane from the drowning liquor would detrimentally affect the properties of the PNC. A small-scale batch was processed through the drowning step, and the resulting mixture was placed under vacuum (50 to 100 mm Hg absolute pressure) and heated in a hot bath to 55° C until all of the nitromethane was removed. The PNC was recovered by centrifuging. Analysis showed it to be the same as conventionally recovered PNC.

Dispersion of Other Propellant Ingredients In PNC

In propellant processing, difficulties are occasionally encountered in obtaining uniform distribution of all propellant ingredients during mixing. It is especially important, yet difficult, to achieve maximum dispersion of ballistic modifiers which are added to the propellant mixes in small quantities. From the comparative ease of dispersing PNC in propellants, the concept of including solids within the small nitrocellulose particles of PNC developed.

Small-scale laboratory tests were made to disperse Carbolac No. 1, a ballistic modifier, within the PNC. A small batch of PNC was processed containing 10% Carbolac No. 1, and another batch was run using 5%. This was accomplished by slurring the almost colloidal Carbolac solids in the nitromethane solvent before adding the nitrocellulose to make the lacquers. The lacquers were then processed by the standard procedures of emulsification and water drowning.

Product was removed by centrifuging and then dried. All of the nitrocellulose and Carbolac were recovered. Microscopic examination showed the particles to be similar in shape to conventional PNC, being spherical with the bulk ranging from 1 to 30 microns in diameter.

A disclosure of invention (Navy Case No. 54, 752) has been submitted for patent application covering the dispersion of finely divided solids within small, essentially spherical particles of nitrocellulose. The solids may be ballistic modifiers, oxidizers, fuels, or other ingredients or mixture of ingredients that are desired in the final propellant and that are compatible with nitrocellulose and other processing materials. Of course, the size of the finely divided solid, must be significantly smaller than the size of the modified nitrocellulose particle desired.

Computer Simulation

Computer studies were performed on both the drown distillation operations and mix compositions by analyzing the thermodynamics and material balances of the overall planned system under various process conditions. A schematic representation of the process delineating the process flow streams subjected to computer analysis in a nitromethane-water system is shown in Figure 3. The computer runs of the system with condensate (stream 13) collection temperatures at 30° C (Table A-I), 25° C (Table A-II), 20° C (Table A-III), 15° C (Table A-IV), and 10° C (Table A-V) are given in Appendix A. For these calculations, the water content of the nitromethane recovery column bottoms was assumed to be 0.1%. The calculated compositions assuming the recovery column bottoms water content to be 0.05% are shown in Table A-VI. The nitromethane content of the drown column bottoms was then reduced from the previously assumed 0.1% to 0.05% (Table A-VII). In Tables A-VIII and IX, the nitromethane column bottoms water content was reduced to 0.02% and 0.01%, respectively, while assuming a drown column bottoms nitromethane content of 0.05%. These data show that process heat duty may be reduced by collecting the azeotrope at the lowest temperature consistent with processing technology. If processing conditions require high purity in either of the distillation columns, process heat duty will go up.

A second computer program was performed to determine the flow stream compositions when either hexane or heptane is used as a drowning medium. A schematic representation of the hydrocarbon drowning process is shown in Figure 4. The tabulated data developed for the hexane-nitromethane-water system are given in Appendix B, and Appendix C presents the data for the heptane-nitromethane-water system.

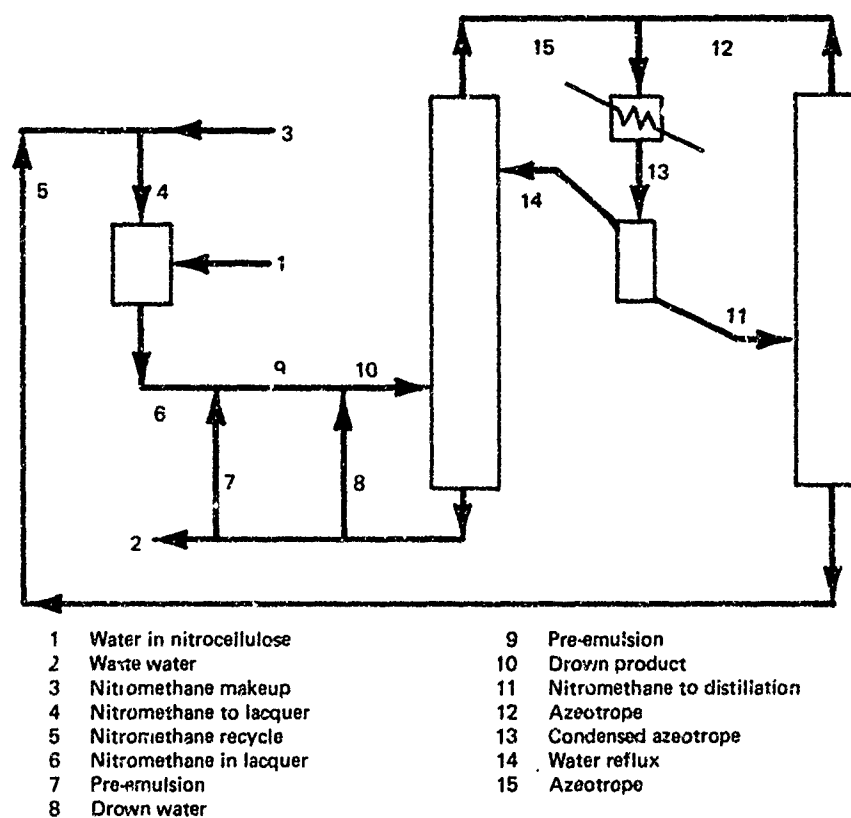


FIGURE 3. COMPUTER FLOW DIAGRAM
OF BINARY SYSTEM

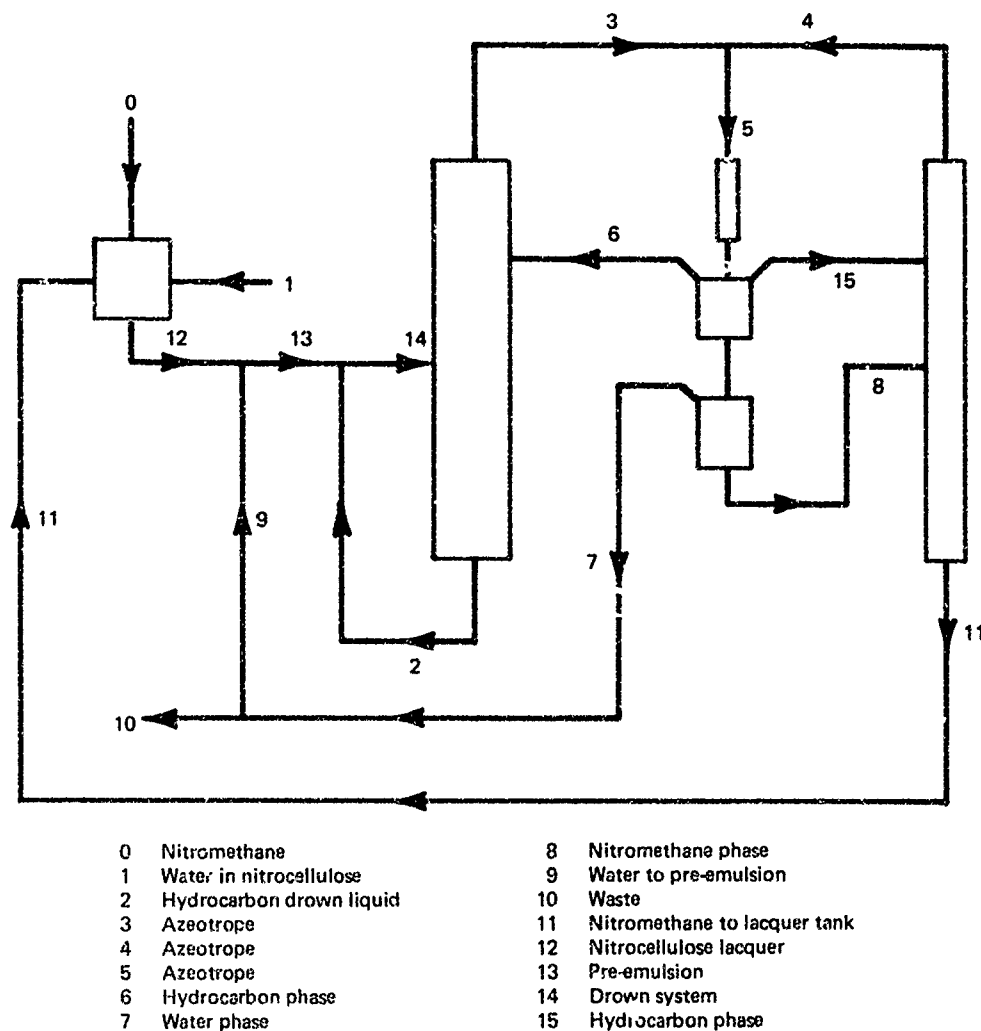


FIGURE 4. COMPUTER FLOW DIAGRAM OF TERNARY SYSTEM

Processing Studies

Studies were made using different types of emulsifying equipment. Several were found capable of making pelletized nitrocellulose.

The standard unit which has been used at Indian Head in batch processing is a Charlotte Colloid Mill, Model ND-20, manufactured by Chemicoloid Laboratories, Inc. This mill emulsifies the feed by high-speed shear action created between a slightly conical rotor and stator seat, each having longitudinal grooves. The clearance between the rotor and stator is adjustable. The colloid mill is large and has relatively high power requirements.

Satisfactory product was made on an experimental scale by a Rapisonic Model Sonolator manufactured by Sonic Engineering Corp. In this unit, an emulsion is produced by mechanically generated, ultrasonic, acoustic energy. Liquid being processed is pumped through a special orifice forming a flat, high-pressure jet stream. This stream impinges on the edge of a blade, or reed, causing ultrasonic vibrations within the liquid. Violent local pressure changes caused by continuous cavitation emulsifies the liquid. Micrometer control of the blade-to-orifice distance is used to vary the amount of acoustic input (and, hence, the level of emulsification) to the material being processed. Because of its relative complexity, this machine was not adopted for plant use.

The machine selected for the continuous facility was the Gifford-Wood Pipe Line Homo-Mixer. It is a compact emulsifier in which a conical rotor having a slope of about 45° can be varied in distance from the stator surface. The stator is ringed with 1/8-inch holes. The rotor revolves at 10,000 rpm imparting high mechanical and hydraulic shear to the feed ingredients. This homogenizer was used in the semicontinuous pilot plant to produce over 17,000 pounds of PNC.

Surfactant studies were conducted concurrent with small batch tests using different types of emulsifying agents. The surfactant that has been used in the batch PNC process is Petromix No. 9, manufactured by Sonneborn Division of Witco Chemical Corp. It is a hydrocarbon sulfonate and is a by-product of petroleum refining. The alkyl sulfonates are anionic surfactants (become negatively charged when ionized). Another commercial sulfonated hydrocarbon, in addition to Petromix, was evaluated in this program. This compound is Sulfatate B-1 and is manufactured by Glycol Chemicals. Although it was suitable for the pre-emulsion, it demonstrated undesirable characteristics when dawning (quenching) was attempted resulting in sticky and fibrous product. The PNC produced using a third surfactant, G-3300 (Atlas Chemical Industries), compared favorably with Petromix. The G-3300 is an amine salt of an alkyl aryl sulfonate.

The investigation of various surfactants was curtailed when it was discovered that an acceptable emulsion and product could be made without surfactant, as described in U. S. Patent No. 3,671,515. This process was developed and proven in the semicontinuous PNC pilot plant. Elimination of surfactant greatly reduces product contamination.

PNC PLANT CONSTRUCTION

A building originally constructed for recovering spent acid from the now inactive nitroguanidine plant was selected for installation of the continuous pelletized nitrocellulose process system. Framing capable of supporting heavy equipment, availability of utilities, and its accessibility for handling materials made the building well suited.

The preliminary design work was done by Station personnel. To prepare a design package for advertisement, an architect-engineering firm was employed (Nathan C. Hale Associates, Falls Church, Va.). Since the only bid received for plant installation exceeded the government estimate by 70% and the available funds, the decision was made to install the process system by Indian Head personnel. Work was started in October 1969.

In order to keep within funding limits, maximum use was made of on-Station, surplus major equipment items and instrumentation. Modifications, which were relatively minor, were made as necessary. Other than a few pumps and the emulsifier, the only large item purchased was a lacquer mix tank. All process lines and equipment were of stainless steel construction to minimize product contamination and avoid corrosion. A hot water generating system was installed to supply heat to the lacquer mix tank through a jacket and for tracing long lacquer and emulsion feed lines. The down column reboiler and the general distillation condenser are large shell and tube, single-pass heat exchangers.

The down column contains 13 trays with 36 bubble caps per tray. The nitromethane recovery column contains an internal double-pass tube heat exchanger. This column is packed with ceramic saddles.

Equipment and general process checkout was started in July 1970. System adjustments and corrections were made in August and September. Basic distillation operating tests then were conducted using nitromethane-water mixtures for feed material. In December, PNC manufacturing studies were attempted.

PRELIMINARY OPERATING STUDIES

In both the distillation and PNC manufacturing areas, design and equipment deficiencies were found which prevented sustained continuous operation.

To prepare the lacquer, dissolution of the nitrocellulose in nitromethane required more than 3 hours in lieu of an anticipated 1 hour. Minimum benefits were obtained from the multiblade turbine agitator in the baffled mix tank. Transferring the lacquer from the mix tank to the unheated feed tanks and holding the material in the feed tanks for even short periods of time caused a loss in temperature and an increase in lacquer viscosity. This created further pumping and processing difficulties. The material was transferred to the feed tanks by nitrogen pressurization of the mix tank. The high nitrogen gas requirement was found to be uneconomical. The lacquer was metered from the feed tanks to the emulsifier by a duplex diaphragm pump. The pulsating action of the lacquer feed caused uneven emulsification of lacquer in water. This resulted in the formation of fibrous-like agglomerates of various sizes during drowning which were carried along in the slurry stream. Entrance of these particles into the drown column could not be prevented in the original installation because the emulsifier and drowning tee were located next to the column feed nozzle.

Cyclone separators were originally installed for concentrating the solids in the slurry prior to final product recovery by centrifugation. These cyclones proved to be unsatisfactory as they could not separate PNC particles under 5 microns from the main fluid stream.

The available column installed as the drown column previously had been used in a nitric acid plant as a fume absorber tower. As such, it had been designed to handle high gas flows. Because of this, only a small single downcomer was present on each tray and liquid distillation capacity was relatively limited. The condenser system which was mutual to both the drown column and the nitromethane recovery column was found to be marginal. The steam available (5 psig) for the reboilers of both columns was insufficient to obtain satisfactory boil-up at the planned process flow rates. Finally, it became evident that additional temperature and steam flow control instrumentation would be required to establish satisfactory column control capability.

Temporary modifications were made to the process system for test purposes to isolate and correct minor deficiencies and to obtain characteristic processing and product data. A plastic line was connected directly from the lacquer mix tank to the lacquer feed pump by-passing the unheated feed tanks. The drowning line was disconnected from the drown column and extended by a flexible line from the drowning tee to open 55-gallon drums. A series of runs was made by the following method.

The down column was filled with fresh water to the high level mark, and the water was circulated through the reboiler to obtain a normal operating temperature. Heated lacquer and pre-emulsion water were pumped to the emulsifier. Down water was pumped, as designed, from the down column via the cyclone separators to the drowning tee. The supply of water available in the column allowed 6 to 8 minutes of operation. The product and process lines were examined after each run. Through a series of modifications to the pre-emulsion and down mixing tees and changes in the size and configuration of the drowning line, product agglomeration was substantially reduced. Further improvement in product quality was achieved through optimization of the process variables of flow and temperature. In later runs, the PNC was recovered by drawing the slurry back into the evacuated down column. From the column, the slurry was pumped to the separation system. Finally, efforts were made to simulate design operating conditions by feeding to a drum and simultaneously withdrawing the slurry to the down column at the feed plate. Screen filters were placed over the down line outlet and the column feed line inlet. Approximately 5 pounds of PNC were recovered at the centrifuge during the final run of the series (no. 18). This run was conducted over a 20-minute period. Accumulation of flocculant material on the filter screens eventually caused the termination of the run. As determined by micromerograph, the mean particle size of the PNC recovered from run no. 18 was 23 microns.

System Revisions

After the final run of this preliminary series, process design modifications were immediately undertaken to incorporate the changes found necessary. Other process improvements and refinements were taken from the semicontinuous PNC pilot plant that had been producing PNC to meet demands during this period. In addition, valuable technical assistance was provided by Commercial Solvents Corp. concerning the details and techniques of nitromethane distillations.

The two small lacquer feed tanks were replaced with two larger, jacketed tanks equipped with agitators. One of these tanks was installed as a second lacquer mix tank, and the other tank was installed as a single lacquer feed tank. A lacquer circulating pump was installed between the lacquer tanks to aid in the dissolution of the nitrocellulose and to pump lacquer to the feed system. The nitrogen pressurization system no longer required for lacquer transfer was removed.

The diaphragm-type lacquer feed pump was replaced with a rotary-type, positive-displacement pump to eliminate pulsing of the feed. The emulsifier was relocated next to the lacquer pump to facilitate startup and shutdown procedures and to eliminate the long, heated lacquer transfer line. Two small tanks were installed in series after the drowning tee to provide sufficient residence of the PNC in drowning and to provide a simple means of filtering out occasional large, abnormal agglomerates of nitrocellulose. Also, basket-type filters were installed in the lacquer circulating and lacquer feed lines as well as in the PNC-water slurry line. A pump was installed to pump the drown slurry from the second drown tank to the drown column. The lacquer mix and the feed tanks, emulsifier, drown tanks, and associated transfer piping (lacquer mix and drown feed subsystem) are shown in Figure 5.

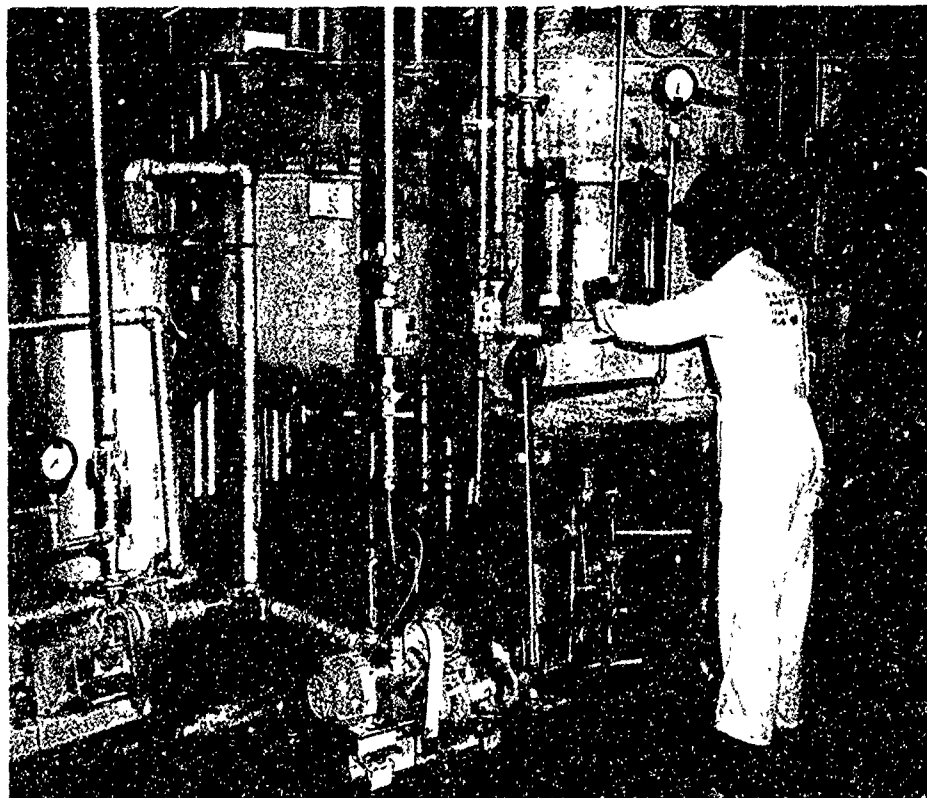


FIGURE 5. NITROCELLULOSE LACQUER PREPARATION
EMULSIFICATION, AND DROWNING

As part of the process revisions, the down column was disassembled and cleaned. Large segmental downcomers were installed on each tray before re-assembly. The piping of the original reboiler was altered so that it could be used as an additional condenser. Another available heat exchanger was installed for the column reboiler. A larger decanter system was installed to improve condensate layer separation and reflux control. The steam supply available for both the down column and the nitromethane recovery column was increased from 5 to 15 psig. New multipoint temperature recorders were installed to monitor the temperature profiles of each column. A general view of a portion of the solvent recovery area is shown in Figure 6.

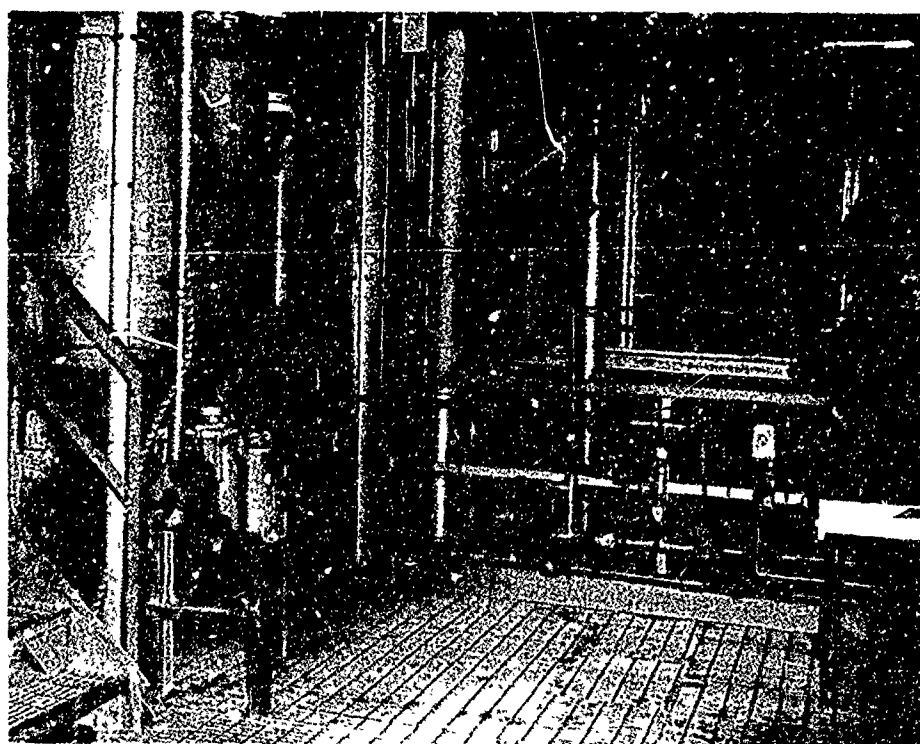


FIGURE 6. SOLVENT RECOVERY AREA

The two cyclone separators used for thickening the PNC slurry were replaced with a disc bowl-type centrifugal clarifier (Figure 7). This centrifuge, while producing a slurry of about the same relative concentration as the cyclones, yields a virtually clear effluent. The retention of PNC fines in the feed to the product separator (Figure 8) ensures the collection of material having an average particle size in the desired lower range.

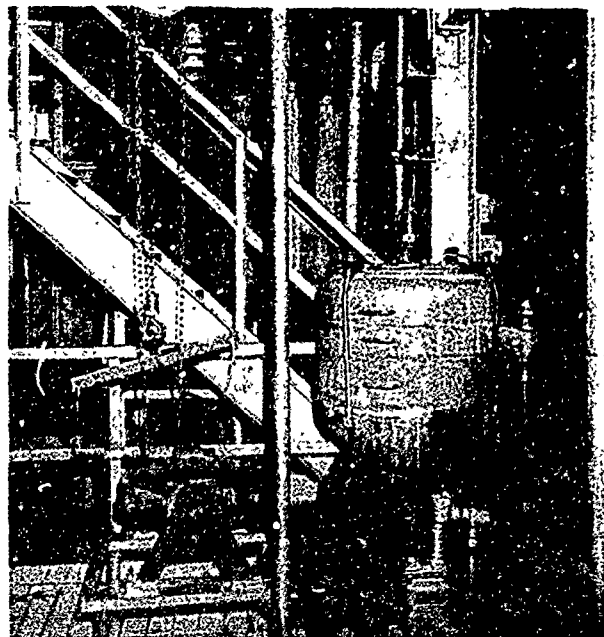


FIGURE 7. PNC SLURRY
CENTRIFUGAL CLARIFIER



FIGURE 8. PNC PRODUCT SEPARATOR
AND FILTRATE TANK

A valve manifold system was installed at the junction of major process lines to provide a means for alternate modes of processing. As a pilot facility, maximum operational flexibility for further experimentation was desired. The following are some of the processing options that have been made possible by the valving arrangement:

(1) Emulsion water source:

- Fresh water (with or without a surfactant)
- Filtrate from product separation
- Water-rich layer from distillation decanter

(2) Drown water source:

- Fresh water
- Filtrate from product separation
- Drown column bottoms
- Storage tanks

(3) Drown slurry feed:

- To drown column
- To product separation
- To storage tanks

(4) Drown column feed source:

- Drown slurry from drown tanks
- Filtrate from product separation
- Filtrate or drown slurry from storage tanks

(5) Drown column bottoms discharge:

- To product separation
- To storage tanks
- To drown water

(6) Product separation feed source:

- Drown slurry
- Drown column bottoms
- Slurry from storage tanks

Finally, rotameters were installed in the emulsion water, drown water, drown column feed, drown column reflux, and nitromethane column feed lines to provide accurate control and processing information.

MANUFACTURING STUDIES

Process equipment and system checkout was performed in August 1972. PNC manufacturing studies were started on 1 September. No major problems nor significant process deficiencies were encountered.

The initial PNC batches were processed using the conventional continuous manufacturing methods originally developed in semicontinuous pilot facility, i.e., using fresh water for drowning and recovering product directly from the drown water slurry. A systematic, step-by-step approach toward complete checkout and full utilization of the new process was made including water and solvent recovery and their reuse. Since starting with the eighth lacquer batch, all of the PNC produced was processed by feeding the drown slurry to the first distillation column and centrifuging the slurry from the column bottoms for product collection. This has provided PNC free of residual solvent. Emulsion water, drown water, and solvent have been continuously recycled within a closed system. A portion of the process water is purged from the system having been displaced by the fresh water used to periodically flush the separation system. This purge has prevented the accumulation of water soluble impurities. The nitromethane solvent is naturally purified during recovery by distillation. No surfactant has been required, nor used, in the PNC manufacture.

By 26 October 1972, a total of 3,404 pounds of PNC had been produced. The overall average nitrocellulose recovery was 94.5%. The nitrocellulose recovery since processing began with the eighth batch using a closed system averaged 96.4%. All of the PNC produced to date in the new facility has conformed to the specifications of WS 12799. Process variables have been studied between PNC manufacturing rates of 31.5 and 40.0 pounds per hour.

The overall system, essentially the nitromethane recovery column, the decanter, and the lacquer preparation/feed area, contains an approximate working level of 8,500 pounds of nitromethane. The system was filled to this working level with nitromethane recovered from the filtrate of the initial PNC batches processed. A total of 10,000 pounds of nitromethane was added to the overall system through the processing of the first 26 batches. For solvent recovery evaluation purposes, only that solvent makeup added since the ninth batch up through the twenty-sixth batch was considered. The amount of nitromethane added during this period was 1,000 pounds. On this basis, solvent recovery is 98%. The moisture content of recovered nitromethane has averaged approximately 0.02%. (Fresh nitromethane moisture content ranges from 0.01% to 0.07%.) Periodic gas chromatographic analyses (Figure 9) show no change in the nitromethane other than a decline in the concentration of nitroparaffin contaminants existing in the fresh (as purchased) material.

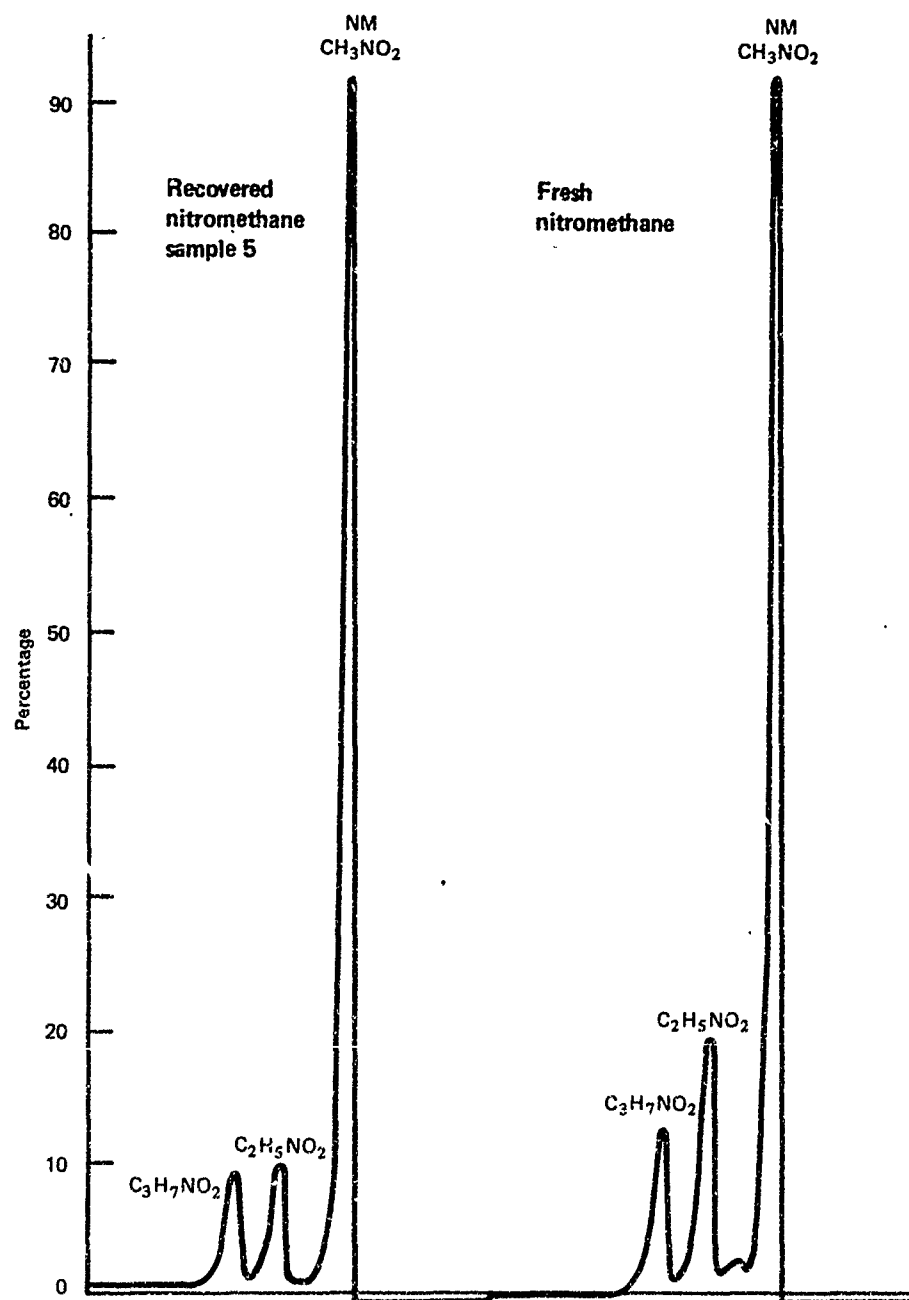


FIGURE 9. NITROMETHANE CHROMATOGRAPHIC ANALYSIS

The first 17 batches of PNC were produced from a lot of nitrocellulose having a viscosity of 11 seconds. Nitrocellulose having a 6-second viscosity was used in the succeeding batches. All of the nitrocellulose used had a nitrogen content of 12.6%.

The limited number of runs under different operating conditions are insufficient for complete evaluation of process variables. However, the indicated effects of general processing changes are given below:

(1) Using filtrate (containing product fines, but solvent free) for drown water - no evident effect on PNC particle size or other characteristics as determined by routine analysis

(2) Using 5% to 8% nitromethane in emulsion water (by blending decanter water layer and filtrate) - elimination of agglomerate formation and periodic plugging of the emulsifier

(3) Use of lower viscosity nitrocellulose - approximate average reduction in mean particle size of 3 to 4 microns.

(4) Lacquer feed rate changes - affects particle size but needs continued study for optimization

(5) Elimination of residual nitromethane in product by feeding slurry to drown column - elimination of product particle adhesion and reduction in solvent losses.

The major effect accomplished by replacing the cyclone separators with a centrifugal clarifier has been that the collection of PNC fines is significantly increased during separation. Hence, the mean particle size of the product has been lowered. Furthermore, use of the clarifier has resulted in a 10% reduction of product lost in filtrate purged from the system.

At this time, only preliminary data and statistical information have been obtained concerning the use of this new product in actual propellant and explosive formulations. Initial data indicate that the new material used in PBXN-103 explosive significantly improves the mechanical properties of the explosive. WS 12800 requires a minimum tensile strength of 60 psi. The tensile strength obtained with the new PNC has been in excess of 100 psi. The overall average in tensile strength previously obtained was approximately 80 psi.

As desired, a decrease in curing time of the PBXN-103 explosive appears to occur through use of the new PNC in the formulation. Some exploration of the plasticization of the new PNC with advanced and experimental materials has also been conducted. For example, the combination of the new PNC with sorbitol pentanitrate in formulating Pentasorb propellant has been successfully achieved.

A summary of the most significant processing data for PNC batches 2A001 through 2B026 is given in Table III; a summary of the applicable analytical data is given in Table IV. Operating sheets of a typical run in the new continuous PNC process are given in Appendix D. A micromerograph particle size distribution plot for a typical PNC batch is given in Figure 10.

Table III
PNC MANUFACTURE PROCESSING DATA

PNC batch	Nitrocellulose used ¹ (lb)	PNC ¹	Nitromethane added (lb)	Drown water source	Nitromethane source	Drown column feed source	Average production rate (lb/hr)
<u>Nitrocellulose Lot 2234 - 11 Second Viscosity</u>							
CX ²	20	14	500	Fresh	Fresh	Filtrate	—
2A001	82.5	53.6	1500	Fresh	Fresh	Filtrate	31.5
2A002	82.5	65.5	1500	Fresh	Fresh	Filtrate	31.9
2A003	165	141	3000	Recovered	Fresh	Filtrate	38.6
2A004	110	136	2000	Recovered	Fresh	Filtrate	37.4
2A005	82.5	75	—	Fresh	Recovered	Filtrate	34.3
2A006	82.5	34.6	500	Fresh	Recovered	Filtrate	34.7
2A007	82.5	93	—	Fresh	Recovered	Slurry	34.2
2A008 ³	165	161	—	Recovered	Recovered	Slurry	35.2
2A009 ⁴	82.5	0	—	Recovered	Recovered	Slurry	—
2A010 ⁵	82.5	142	—	Recovered	Recovered	Slurry	34.0
2A011	165	97	500	Recovered	Recovered	Slurry	35.3
2A012	82.5	139	—	Recovered	Recovered	Slurry	34.7
2A013	165	182	—	Recovered	Recovered	Slurry	35.7
2A014	82.5	97	—	Recovered	Recovered	Slurry	35.2
2A015	165	149.5	—	Recovered	Recovered	Slurry	35.6
2A016	82.5	105.5	—	Recovered	Recovered	Slurry	35.9
2A017	165	105.5	—	Recovered	Recovered	Slurry	37.6
<u>Nitrocellulose Lot 2246 - 6-Second Viscosity</u>							
2B018 ⁶	165	130.5	—	Recovered	Recovered	Slurry	35.4
2B019	185	199.2	—	Recovered	Recovered	Slurry	36.2
2B020	247.5	239	500	Recovered	Recovered	Slurry	36.8
2B021	82.5	55	—	Recovered	Recovered	Slurry	36.2
2B022	247.5	187	—	Recovered	Recovered	Slurry	35.6
2B023	165	239	—	Recovered	Recovered	Slurry	37.2
2B024	247.5	210	—	Recovered	Recovered	Slurry	40.0
2B025	194	167.5	—	Recovered	Recovered	Slurry	35.3
2B026	165	131.8	—	Recovered	Recovered	Slurry	31.0

¹ Batch nitrocellulose usage and PNC production are not directly comparable because of in process inventory fluctuations.

² Batch CX was processed to clean out the systems.

³ Batch 2A008 was the first batch to be processed using all recovered solvent and water.

⁴ Batch 2A009 product (15 lb) was blended with the PNC from batch 2A013.

⁵ Batch 2A010 contained lacquer left from batch 2A009.

⁶ Batch 2B018 was the first batch to be processed using lower viscosity nitrocellulose (6 second).

Table IV
PNC MANUFACTURE ANALYTICAL DATA

PNC batch	Total Volatiles (%)	Particle size (μ)	Viscosity (sec)	Stabilizer (%)
2A001	49.5	14.2	2	3.5
2A002	46.6	13.8	3	—
2A003	43.5	16.4	1	—
2A004	41.5	14.5	3	—
2A005	45.5	12.5	3	3.83
2A006	50.5	12.1	3	4.4
2A007	43.2	12.7	12	4.1
2A008	39.2	13.3	5	—
2A009 ¹	—	—	—	—
2A010	39.6	15.1	5	—
2A011	32.5	14.2	12	—
2A012	39.6	14.0	12	—
2A013	39.7	15.3	4	—
2A014	38.5	15.3	3	—
2A015	38.9	12.6	9	—
2A016	40.3	14.5	2	3.7
2A017	36.1	18.7	1	—
2A018	40.5	11.7	4	3.8
2B019	40.2	9.7	2	—
2B020	40.3	9.8	4	—
2B021 ¹	39.1	—	—	—
2B022	45.2	11.8	3	—
2B023	44.5	11.7	3	3.6
2B024	42.7	11.3	7	—
2B025	43.2	12.0	6	3.4
2B026	47.1	12.1	6	3.6

¹ Batches 2A009 and 2B021, being small, were set aside for later blending and therefore not separately analyzed.

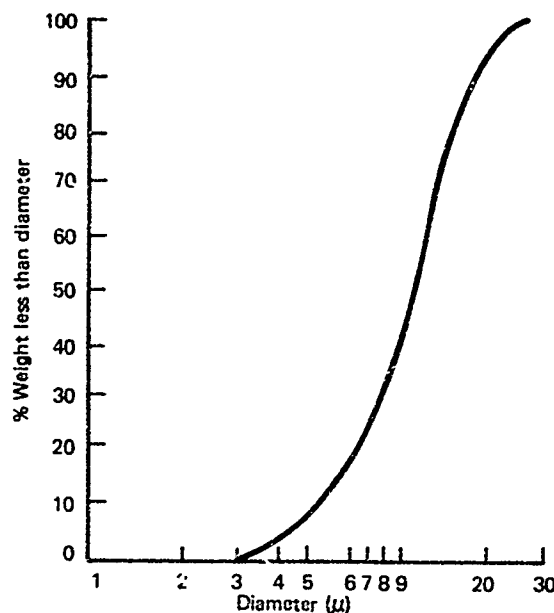


FIGURE 10. PARTICLE SIZE
DISTRIBUTION ANALYSIS OF PNC

CONCLUSIONS

The feasibility of producing pelletized nitrocellulose through the continuous formation of a nitrocellulose lacquer-water emulsion, the continuous drowning or quenching of the emulsion, and the removal of the solvent from the product by feeding the resulting slurry directly to a distillation column was demonstrated in laboratory and small-scale studies.

Based on these studies, a continuous pelletized nitrocellulose facility has been installed at the Naval Ordnance Station, Indian Head, Maryland. The facility was established largely with surplus parts and equipment to keep installation costs within the limits of available funding. Initial pilot studies showed that several process equipment items required modifications or replacement in order to achieve sustained, continuous operating capability.

After making the necessary process corrections, operations were resumed in September 1972. No significant problems, thereafter, were encountered. The major achievements have been the virtual elimination of pollutants to the environment and a greater than 75% reduction in PNC manufacturing costs through the recovery and recycle of solvent and water filtrate containing product fines.

The manufacture of PNC in this new process is being continued to provide material for current requirements. All of the PNC produced has met Weapons Specification 12799. The average production rate has slightly exceeded the estimated capacity of 35 pounds per hour.

The plant capacity can be doubled, through relatively minor equipment additions and process modifications to further reduce product manufacturing costs.

Under a separate project, the design criteria has been established for 750-pound per hour, fully automated, PNC plant. Consideration is being given to the timely construction of the large facility.

Appendix A

WEIGHT FRACTION OF COMPONENTS:
BINARY SYSTEM

Table A-I

COMPUTER ANALYSIS WITH CONDENSATE COLLECTION AT 30° C¹

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1.0	0	20	0	20
2	0.999	0.001	20	0.02002	20.02
3	0	1.0	0	0.02002	0.02002
4	0.000999988	0.999	1.81998	1818.18	1820
5	0.001	0.999	1.81998	1818.16	1819.98
6	0.0118587	0.988141	21.82	1818.18	1840
7	0.999	0.001	1181.82	1.183	1183
8	0.999	0.001	63384	63.4474	63447.4
9	0.39816	0.60184	1203.64	1819.36	3023
10	0.971674	0.0283256	64587.6	1882.81	66470.5
11	0.025	0.975	51.3521	2002.73	2054.08
12	0.216	0.784	49.5321	184.569	234.101
13	0.216	0.784	570.353	2070.17	2640.53
14	0.885	0.115	519.001	67.4409	586.442
15	0.216	0.784	520.821	1885.6	2406.42

¹ Assuming recovery column bottoms water content of 0.1% and down column bottoms nitromethane content of 0.1%

Table A-II

COMPUTER ANALYSIS WITH CONDENSATE COLLECTION AT 25° C

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.999	0.001	20	0.02002	20.02
3	0	1	0	0.02002	0.02002
4	0.000999988	0.999	1.81998	1818.18	1820
5	0.001	0.999	1.81998	1818.16	1819.98
6	0.0118587	0.988141	21.82	1818.18	1840
7	0.999	0.001	1181.82	1.183	1183
8	0.999	0.001	63384	63.4474	63447.4
9	0.39816	0.60184	1203.64	1819.36	3023
10	0.971674	0.0283256	64587.6	1882.81	66470.5
11	0.022	0.978	44.491	1977.83	2022.32
12	0.216	0.784	42.671	159.666	202.337
13	0.216	0.784	562.553	2041.86	2604.41
14	0.89	0.11	518.062	64.0301	582.092
15	0.216	0.784	519.882	1882.19	2402.07

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Table A-III

COMPUTER ANALYSIS WITH CONDENSATE COLLECTION AT 20° C

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.999	0.001	20	0.02002	20.02
3	0	1	0	0.02002	0.02002
4	0.000999988	0.999	1.81998	1818.18	1820
5	0.001	0.999	1.81998	1818.16	1819.98
6	0.0118587	0.988141	21.82	1818.18	1840
7	0.999	0.001	1181.82	1.183	1183
8	0.999	0.001	63384	63.4474	63447.4
9	0.39816	0.60184	1203.64	1819.36	3023
10	0.971674	0.0283256	64587.6	1882.81	66470.5
11	0.018	0.982	35.6663	1945.8	1981.46
12	0.216	0.784	33.8464	127.636	161.482
13	0.216	0.784	552.619	2005.8	2558.42
14	0.896	0.104	516.952	60.0034	576.956
15	0.216	0.784	518.772	1878.17	2396.94

Table A-IV

COMPUTER ANALYSIS WITH CONDENSATE COLLECTION AT 15° C

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.999	0.001	20	0.02002	20.02
3	0	1	1	0.02002	0.02002
4	0.000999988	0.999	1.81998	1818.18	1820
5	0.001	0.999	1.81998	1818.16	1819.98
6	0.0118587	0.988141	21.82	1818.18	1840
7	0.999	0.001	1181.82	1.183	1183
8	0.999	0.001	63384	63.4474	63447.4
9	0.39816	0.60184	1203.64	1819.36	3023
10	0.971674	0.0283256	64587.6	1882.81	66470.5
11	0.015	0.985	29.2783	1922.61	1951.89
12	0.216	0.784	27.4584	104.45	131.906
13	0.216	0.784	544.603	1976.71	2521.31
14	0.905	0.095	515.324	54.0948	569.419
15	0.216	0.784	517.144	1872.26	2389.4

Table A-V

COMPUTER ANALYSIS WITH CONDENSATE COLLECTION AT 10° C

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.999	0.001	20	0.02002	20.02
3	0	1	0	0.02002	0.02002
4	0.000999988	0.999	1.81998	1818.18	1820
5	0.001	0.999	1.81998	1818.16	1819.98
6	0.0118587	0.988141	21.82	1818.18	1840
7	0.999	0.001	1181.82	1.183	1183
8	0.999	0.001	63384	63.4474	63447.4
9	0.39816	0.60184	1203.64	1819.36	3023
10	0.971674	0.0283256	64587.6	1882.81	66470.5
11	0.012	0.988	23.0782	1900.11	1923.19
12	0.216	0.784	21.2582	81.9454	103.204
13	0.216	0.784	537.869	1952.27	2490.14
14	0.908	0.092	514.791	52.1595	566.951
15	0.216	0.784	516.611	1870.32	2386.93

Table A-VI

COMPUTER ANALYSIS ASSUMING RECOVERY COLUMN BOTTOMS WATER CONTENT OF 0.05% AND DROWN COLUMN BOTTOMS NITROMETHANE CONTENT OF 0.1%

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.999	0.001	20	0.02002	20.02
3	0	1	0	0.02002	0.02002
4	0.000499994	0.9995	0.909534	1818.18	1819.09
5	0.0005	0.9995	0.909534	1818.16	1819.07
6	0.0113695	0.988631	20.9095	1818.18	1839.09
7	0.999	0.001	1181.82	1.183	1183
8	0.999	0.001	63384	63.4474	63447.4
9	0.397978	0.602022	1202.73	1819.36	3022.09
10	0.971674	0.0283259	64586.7	1882.81	66469.5
11	0.012	0.988	23.0898	1901.06	1924.15
12	0.216	0.784	22.1803	82.8979	105.078
13	0.216	0.784	538.139	1953.25	2491.38
14	0.908	0.092	515.049	52.1856	567.235
15	0.216	0.784	515.959	1870.35	2386.31

Table A-VII

COMPUTER ANALYSIS ASSUMING RECOVERY COLUMN BOTTOMS WATER
CONTENT OF 0.05% AND DROWN COLUMN BOTTOMS NITROMETHANE
CONTENT OF 0.05%

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.9995	0.0005	20	0.010005	20.01
3	0	1	0	0.010005	0.010005
4	0.000499997	0.9995	0.90954	1818.18	1819.09
5	0.0005	0.9995	0.90954	1818.17	1819.08
6	0.0113695	0.988631	20.9095	1818.18	1839.09
7	0.9995	0.0005	1181.82	0.591204	1182.41
8	0.9995	0.0005	63384	31.7078	63415.7
9	0.398056	0.601944	1202.73	1818.77	3021.5
10	0.972147	0.0278531	64586.7	1850.48	66437.2
11	0.012	0.988	23.0899	1901.07	1924.16
12	0.216	0.784	22.1804	82.8983	105.079
13	0.216	0.784	538.142	1953.26	2491.4
14	0.908	0.092	515.052	52.1859	567.238
15	0.216	0.784	515.962	1870.36	2386.32

Table A-VIII

COMPUTER ANALYSIS ASSUMING RECOVERY COLUMN BOTTOMS WATER
CONTENT OF 0.02% AND DROWN COLUMN BOTTOMS NITROMETHANE
CONTENT OF 0.05%

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.9995	0.0005	20	0.010005	20.01
3	0	1	0	0.010005	0.010005
4	0.000199999	0.9998	0.363707	1818.18	1818.55
5	0.0002	0.9998	0.363707	1818.17	1818.54
6	0.011076	0.988924	20.3637	1818.18	1838.55
7	0.9995	0.0005	1181.82	0.591204	1182.41
8	0.9995	0.0005	63384	31.7078	63415.7
9	0.397948	0.602052	1202.18	1818.77	3020.95
10	0.972147	0.0278533	64586.2	1850.48	66436.7
11	0.012	0.988	23.0969	1901.64	1924.74
12	0.216	0.784	22.7331	83.4693	106.202
13	0.216	0.784	538.304	1953.84	2492.15
14	0.908	0.092	515.207	52.2016	567.408
15	0.216	0.784	515.57	1870.37	2385.94

Table A-IX

COMPUTER ANALYSIS ASSUMING RECOVERY COLUMN BOTTOMS WATER
CONTENT OF 0.01% AND DROWN COLUMN BOTTOMS NITROMETHANE
CONTENT OF 0.05%

Stream	Weight fraction		Weight (lb/hr)		Total weight
	Water	Nitromethane	Water	Nitromethane	
1	1	0	20	0	20
2	0.9995	0.0005	20	0.010005	20.01
3	0	1	0	0.010005	0.010005
4	0.0000999993	0.9999	0.181835	1818.18	1818.36
5	0.0001	0.9999	0.181835	1818.17	1818.35
6	0.0109782	0.989022	20.1818	1818.18	1838.36
7	0.9995	0.0005	1181.82	0.591204	1182.41
8	0.9995	0.0005	63384	31.7078	63415.7
9	0.397911	0.602089	1202	1818.77	3020.77
10	0.972147	0.0278534	64586	1850.48	66436.5
11	0.012	0.988	23.0992	1901.83	1924.93
12	0.216	0.784	22.9173	83.6596	106.577
13	0.216	0.784	538.357	1954.04	2492.4
14	0.908	0.092	515.258	52.2068	567.465
15	0.216	0.784	515.44	1870.38	2385.82

Appendix B
FLOW STREAM COMPOSITIONS WITH HEXANE:
TERNARY SYSTEM

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Table B-I
WEIGHT FRACTION OF COMPONENTS WITH HEXANE

Stream	Hexane	Nitromethane	Water
0	0	1	0
1	0	0	1
2	0.995	0.002	0.003
3	0.852	0.123	0.025
4	0.852	0.123	0.025
5	0.852	0.123	0.025
6	0.9708	0.0292	0
7	0	0.103	0.897
8	0.0158	0.9567	0.0275
9	0	0.103	0.897
10	0	0.103	0.897
11	0	0.998	0.002
12	0	0.987165	1.28346
13	0	0.618447	0.381553
14	0.857422	8.72357	5.53423
15	0.9708	0.0292	0

Table B-II
FLOW RATES OF COMPONENTS IN POUNDS PER HOUR WITH HEXANE

Stream	Hexane	Nitromethane	Water	Total
0	0	2.29654	0	2.29654
1	0	2	20	20
2	19591.4	39.3797	59.0696	19689.9
3	41082	5930.85	1205.46	48218.3
4	1864.6	269.185	54.7124	2188.5
5	42946.6	6200.03	1260.17	50406.8
6	41082	1235.68	0	42317.7
7	0	138.001	1201.82	1339.82
8	33.5256	2029.99	58.3515	2121.87
9	0	135.705	1181.82	1317.52
10	0	2.29654	20	22.2965
11	0	1815.89	3.63905	1819.52
12	0	1818.18	23.639	1841.82
13	0	1953.89	1205.46	3159.34
14	19591.4	1993.27	1264.53	22849.2
15	1831.07	55.0756	0	1886.15

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Table B-III

MOLE FRACTION OF COMPONENTS WITH HEXANE

Stream	Hexane	Nitromethane	Water
0	0	1	0
1	0	0	1
2	0.980326	3.23468	1.64391
3	0.714194	0.169252	0.116554
4	0.714194	0.169252	0.116554
5	0.714194	0.169252	0.116554
6	0.952948	4.70517	0
7	0	3.27804	0.96722
8	9.08456	0.902975	8.79405
9	0	3.27804	0.96722
10	0	3.27804	0.96722
11	0	0.993256	6.74399
12	0	0.957808	4.21917
13	0	0.323593	0.676407
14	0.65531	0.109446	0.235244
15	0.952948	4.70517	0

Table B-IV

FLOW RATES OF COMPONENTS IN MOLES PER HOUR WITH HEXANE

Stream	Hexane	Nitromethane	Water	Total
0	0	3.76236	0	3.76236
1	0	0	1.11012	1.11012
2	195.523	0.645146	3.27873	199.447
3	410	97.1633	66.9104	574.074
4	18.6088	4.40998	3.03688	26.0556
5	428.609	101.573	69.9473	600.129
6	410	20.2437	0	430.244
7	0	2.26084	66.7084	68.9692
8	0.334587	33.2568	3.23887	36.8303
9	0	2.22321	65.5983	67.8215
10	0	3.76236	1.11012	1.14775
11	0	29.7491	0.20199	29.9511
12	0	29.7867	1.31211	31.0988
13	0	32.0099	66.9104	98.9203
14	195.523	32.6551	70.1891	298.367
15	18.2742	0.902286	0	19.1765

Table B-V

VOLUME FRACTION OF COMPONENTS WITH HEXANE

Stream	Hexane	Nitromethane	Water
0	0	1	0
1	0	0	1
2	0.996733	1.21230	2.05485
3	0.903001	7.88822	1.81172
4	0.903001	7.88822	1.81172
5	0.903001	7.88822	1.81172
6	0.982125	0.017875	0
7	0	9.22435	0.907757
8	2.57539	0.943597	3.06494
9	0	9.22435	0.907757
10	0	9.22435	0.907757
11	0	0.997741	2.25941
12	0	0.985521	1.44789
13	0	0.589221	0.410779
14	0.904407	5.56787	3.99144
15	0.982125	0.017875	0

Table B-VI

FLOW RATES OF COMPONENTS IN GALLONS PER HOUR WITH HEXANE

Stream	Hexane	Nitromethane	Water	Total
0	0	4.06143	0	4.06143
1	0	0	0.039968	0.039968
2	57.2591	6.96429	0.118045	57.4468
3	120.069	10.4887	2.40899	132.967
4	5.4496	0.476053	0.109337	6.03499
5	125.518	10.9647	2.51832	139.001
6	120.069	2.18529	0	122.254
7	0	0.244055	2.40172	2.64577
8	0.097984	3.59004	0.11661	3.80463
9	0	0.23994	2.36175	2.60174
10	0	4.06143	0.039968	4.40295
11	0	3.21139	7.27228	3.21866
12	0	3.21545	4.72403	3.26269
13	0	3.45544	2.40899	5.86443
14	57.2591	3.53509	2.52703	63.3112
15	5.35161	0.097401	0	5.44902

Appendix C

FLOW STREAM COMPOSITIONS WITH HEPTANE:
TERNARY SYSTEM

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Table C-I

WEIGHT FRACTION OF COMPONENTS WITH HEPTANE

Stream	Heptane	Nitromethane	Water
0	0	1	0
1	0	0	1
2	0.995	0.002	0.003
3	0.656	0.277	0.067
4	0.656	0.277	0.067
5	0.656	0.277	0.067
6	0.977	0.023	0
7	0	0.0948	0.9052
8	0.0029	0.9718	0.0252
9	0	0.0948	0.9052
10	0	0.0948	0.9052
11	0	0.998	0.002
12	0	0.987165	1.28348
13	0	0.617	0.383
14	0.85787	8.67587	5.53712
15	0.9708	0.0292	0

Table C-II

FLOW RATES OF COMPONENTS IN POUNDS PER HOUR WITH HEPTANE

Stream	Heptane	Nitromethane	Water	Total
0	0	2.09456	0	2.09456
1	0	0	20	20
2	19591.4	39.3797	59.0696	19689.9
3	11802.7	4983.76	1205.46	17991.9
4	472.501	199.516	48.2585	720.276
5	12275.2	5183.27	1253.72	18712.2
6	11802.7	277.852	0	12080.5
7	0	125.864	1201.82	1327.68
8	5.97238	2001.57	51.8979	2059.44
9	0	123.77	1181.82	1305.59
10	0	2.09456	20	22.0946
11	0	1816.09	3.63945	1819.73
12	0	1818.18	23.6395	1841.82
13	0	1941.95	1205.46	3147.41
14	19591.4	1981.33	1264.53	22837.8
15	466.529	14.0324	0	480.561

Table C-III

MOLE FRACTION OF COMPONENTS WITH HEPTANE

Stream	Heptane	Nitromethane	Water
0	0	1	0
1	0	0	1
2	0.980326	3.23468	1.64391
3	0.442244	0.306543	0.251213
4	0.442244	0.306543	0.251213
5	0.442244	0.306543	0.251213
6	0.962793	3.72066	0
7	0	2.99838	0.970016
8	1.66813	0.917712	8.06198
9	0	2.99838	0.970016
10	0	2.99838	0.970016
11	0	0.993256	6.74399
12	0	0.957808	4.21924
13	0	0.322253	0.677747
14	0.65574	0.108862	0.235398
15	0.952948	4.70517	0

Table C-IV

FLOW RATES OF COMPONENTS IN MOLES PER HOUR WITH HEPTANE

Stream	Heptane	Nitromethane	Water	Total
0	0	3.43146	0	3.43146
1	0	0	1.11012	1.11012
2	195.523	0.645146	3.27873	199.447
3	117.791	81.6474	66.9104	266.349
4	4.71558	3.26862	2.67865	10.6628
5	122.507	84.916	69.589	277.012
6	117.791	4.55197	0	122.343
7	0	2.062	66.7084	68.7704
8	5.96046	32.7911	2.88066	35.7314
9	0	2.02768	65.5983	67.6259
10	0	3.43146	1.11012	1.14444
11	0	29.7524	0.202012	29.9544
12	0	29.7867	1.31214	31.0989
13	0	31.8144	66.9104	98.7248
14	195.523	32.4596	70.1891	298.172
15	4.65597	0.229888	0	4.88586

Table C-V

VOLUME FRACTION OF COMPONENTS WITH HEPTANE

Stream	Heptane	Nitromethane	Water
0	0	1	0
1	0	0	1
2	0.996733	1.21230	2.05485
3	0.754523	0.192785	5.26923
4	0.754523	0.192785	5.26923
5	0.754523	0.192785	5.26923
6	0.985855	1.40448	0
7	0	8.48189	0.915181
8	4.76797	0.966902	2.83296
9	0	8.48189	0.915181
10	0	8.48189	0.915181
11	0	3.597741	2.25941
12	0	0.985521	1.44792
13	0	0.587737	0.412263
14	0.904709	5.53637	3.99277
15	0.982125	0.017875	0

Table C-VI

FLOW RATES OF COMPONENTS IN GALLONS PER HOUR WITH HEPTANE

Stream	Heptane	Nitromethane	Water	Total
0	0	3.70423	0	3.70423
1	0	0	0.039968	0.039968
2	57.2591	6.96429	0.118045	57.4468
3	34.4953	8.81376	2.40899	45.718
4	1.38096	0.352844	9.64398	1.83025
5	35.8763	9.1666	2.50543	47.5483
6	34.4953	0.491381	0	34.9867
7	0	0.222591	2.40172	2.62431
8	1.74553	3.53977	0.103713	3.66094
9	0	0.218886	2.36175	2.58063
10	0	3.70423	0.039968	4.36723
11	0	3.21174	7.27309	3.21902
12	0	3.21545	4.72411	3.16169
13	0	3.43433	2.40899	5.84532
14	57.2591	3.50398	2.52703	63.2901
15	1.36351	2.48162	0	1.38832

Appendix D
OPERATING SHEETS OF A TYPICAL RUN

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PNC PROCESS SHEET
BLDG. 859

PNC BATCH 28023 DATE 10/17/72
 ENGINEER Geist OPERATOR Cox
 ETHYL CENTRALITE LOT 864
 TANK E2 3.0 LBS. TANK E3 3.0 LBS. TANK E4 — LBS.
 NITROCELLULOSE LOT 2247 MOISTURE 27.7 %
 TANK E2 82.5 LBS. DRY 114.1 LBS. WET
 TANK E3 82.5 LBS. DRY 114.1 LBS. WET
 TANK E4 — LBS. DRY — LBS. WET
 NITROMETHANE LOT — MOISTURE — % NO. FRESH DRUMS —
 TANK E2 FINAL LEVEL 9% MIX — HRS.
 TANK E3 FINAL LEVEL 10% MIX — HRS.
 TANK E4 FINAL LEVEL — MIX — HRS.
 EMULSIFIER None LOT — QUANTITY — cc/in EW
 LACQUER FEED 11.5 LBS/MIN. TEMP 140° F
 COLLOID MILL 10,000 RPM .003 IN. CLEARANCE
 EMULSION WATER ROTA 95 TEMP 115 F % NM 4 TO 8
 DROWN WATER ROTA 50 TEMP 122 F MAX NM 1 %
 DROWN WATER FROM Filtrate Tank FILTRATE TO Drown Water
 RECOVERY SYSTEM PRESSURE 180 MAX DC PRESSURE 240
 DC FEED FROM Drn. Tk. MAX FEED RATE 60 MAX. COND VAPOR TEMP. 150
 DC TEMP. TR61 — TR59 — FEED — TOP —
 DC BOTTOMS TO Clarifier Level 40-100
 NM COL MAX FEED RATE 85 MAX NM COL PRESSURE 330
 NM COL TEMP. BOTTOM — MID — TOP —

FIGURE D-1. EXAMPLE OF PNC PROCESS SHEET

LACQUER PREPARATION SHEET

PNC BATCH NO. 28023DATE 10/17/72LACQUER BATCH 2ENGINEER GeistLACQUER E2OPERATOR CoxNM TANK E1 AT START TIME — LEVEL —NM TANK E1 AT FINISH TIME — LEVEL —NM COLUMN PRODUCTION RATE —FRESH NM USED: LOT NO. None DRUM NOS. —LACQUER TANK AT START LEVEL EmptyEND 1ST NM ADDITION LEVEL 25 TIME 0855 TEMP 130°FETHYL CENTRALITE ADDED WEIGHT 3.0 TIME 0900

NITROCELLULOSE ADDITIONS

WEIGHTS

LOT NO.	DRUM NO.	% MOISTURE	START	FINISH	NET
<u>2247</u>	<u>17</u>	<u>—</u>	<u>111.0</u>	<u>49.1</u>	<u>61.9</u>
<u>2247</u>	<u>2</u>	<u>—</u>	<u>268.6</u>	<u>216.4</u>	<u>52.2</u>
<u>—</u>	<u>—</u>	<u>—</u>	<u>—</u>	<u>—</u>	<u>114.1</u>

END 2ND NM ADDITION LEVEL 9½ TIME 10:30 TEMP 150START CIRCULATION THROUGH E7 TIME 1030 TEMP 136STOP CIRCULATION THROUGH E7 TIME 1205 TEMP 140

TRANSFER TO FEED TANK

	TIME	LACQUER TANK		FEED TANK	
		LEVEL	TEMP	LEVEL	TEMP
START	<u>1205</u>	<u>9½</u>	<u>141</u>	<u>43½</u>	<u>140</u>
FINISH	<u>1220</u>	<u>Empty</u>	<u>—</u>	<u>20</u>	<u>140</u>

FIGURE D-2. EXAMPLE OF LACQUER PREPARATION SHEET

PNC OPERATING SHEET

PNC BATCH 2B023				ENGINEER Geist				OPERATOR Cox				DATE 10/17/72			
LACQUER FEED				EMULSION WATER				DROWN WATER				FILTRATE			
TANK	LEVEL	TEMP	PSIG	ROTA	LEVEL	TEMP	PSIG	ROTA	TEMP	SOURCE	FILTRATE TO	WET PNC	TIME	COMMENTS	
E4	33%	140	10	95	—	118	7½	50	124	F.T.	D.W.	42.0	0945	Start	
E4	48½	138	10	92	—	117	5	50	122	F.T.	D.W.	43.4	1025	Transferred E3	
E4	33	141	10	95	—	118	6	50	120	F.T.	D.W.	44.8	1105		
E4	43½	140	10	95	—	116	4	50	121	F.T.	D.W.	40.2	1145	Transferred E2	
E4	25	138	10	96	—	120	5	50	122	F.T.	D.W.	62.4	1245		
E4	33	140	10	95	—	114	5½	50	122	F.T.	D.W.	55.3	1335		
E4	40½	141	10	95	—	117	5	50	122	F.T.	D.W.	47.0	1415	Transferred E3	
E4	19½	139	10	95	—	115	5	50	122	F.T.	D.W.	44.4	1450		
E4	24	141	10	95	—	119	5	50	122	F.T.	D.W.	51.4		End	
												430.9#			

FIGURE D-3. EXAMPLE OF PNC OPERATING SHEET

TIME	0800	0900	1000	1100	1200	1300	1400	1500
FEED								
SOURCE	D.T.							
ROTA	0	4.5	55	54	54	54	55	56
TEMP 53	-	83	118	119	118	118	119	119
% NM	-	-	-	-	-	-	-	-
REFLUX								
ROTA	90	61	68	72	53	67	70	52
TEMP 54	65	60	56	54	53	52	52	51
OVERHEAD								
PRES 51	223	224	233	235	233	234	234	233
TEMP 55	153	151	150	151	150	151	151	150
CV TEMP 66	62	64	67	68	70	71	71	72
COLUMN - DIFFERENTIAL PRESSURES								
TOP 49	12	14	16	15	16	16	16	16
BOT 50	20	26	26	26	27	26	26	26
TEMPERATURES								
FEED TR	155	155	156	157	156	156	157	156
MID 58	158	157	158	159	158	158	159	158
LOW 59	159	159	160	161	160	160	161	160
BOTTOMS								
LEVEL 63	124	81	69	59	64	83	80	101
VALVE 65	-	5.3	5.2	5.4	6.0	5.0	5.3	5.0
TEMP 61	162	162	163	164	163	163	164	163
PUMP 65								
STEAM 64	10 PSI	max	max	max	max	max	max	max
% NM								
DEST.								
COMMENTS								

FIGURE D-4. EXAMPLE OF DROWN COLUMN OPERATING SHEET

NM COLUMN OPERATING SHEET

ENGINEER Geist

OPERATOR Cox

DATE 10/17/72

[illegible]

COMMENTS

FIGURE D-5. EXAMPLE OF NITROMETHANE COLUMN OPERATING SHEET